

Laboratory Analysis Comparison Mercury Testing in Fish Tissue Samples

Utah Department of Environmental Quality
Utah Division of Water Quality



Lake Powell

Prepared by Amy Dickey and Benjamin Brown
Utah Division of Water Quality
August 2006

Introduction

The presence of mercury in fish tissues is a growing concern. The Utah Division of Water Quality (UDWQ) is rapidly working to determine the extent of the contamination and what implications it might have on the citizens of Utah. Fish consumption advisories were issued in the summer of 2005 for three waterbodies based on analysis of tissue samples collected. Results showed that concentrations of methylmercury were above the EPA criterion of 0.3 mg/kg set to protect public health. Although the lab analyzed for total mercury, that criterion is appropriate as numerous studies have shown that virtually all the mercury found in the edible portion of a fish is methylmercury. In addition, the Utah Division of Wildlife Resources assessed mercury values in waterfowl and issued a consumption advisory on two species of waterfowl, specifically the common goldeneye and northern shoveler in September 2005.

UDWQ began collecting fish tissue samples as part of a comprehensive stream assessment program in 2000. Mercury was just one of numerous parameters measured. Initially, samples were sent out of state for processing because the Utah Department of Health Laboratory (UDOH) was not equipped for mercury analysis. In 2005, UDWQ provided funds for the laboratory to purchase a direct mercury analyzer in an attempt to eliminate the backlog of samples, speed up analysis, and get critical information to the public in a timely manner.

As a quality assurance check for the UDOH laboratory, UDWQ sent duplicate fish tissue samples to four certified environmental laboratories to see how UDOH laboratory results compared to those measured by other laboratories. Cooperating laboratories included:

1. Region 8 Environmental Protection Agency (EPA)
2. Trace Element Research Laboratory at Texas A&M University
3. Arizona Department of Health Services
4. United States Geological Survey (USGS) in Boulder, Colorado.

Methods

Fish were collected by gill netting at four different locations on Lake Powell, a large reservoir located on the Colorado River in southeastern Utah. Sampling was conducted in November, 2005. Five fish (striped bass) were collected at each of the four locations to allow for statistically significant comparisons.

Species, weight, and length were measured and recorded for each fish collected. Each fish was handled with new nitrile gloves to prevent cross contamination. Each individual fish was given a unique identification number, made up of a seven digit STORET number for the site, the fish ID code, and fish sequence number (ex:4956600CTT01). The fish were then wrapped in aluminum foil, labeled with their unique code, and frozen until they were ready to be processed for lab analysis.

Fish tissue for laboratory analysis from each of the collected fish were processed in accordance with UDWQ's SOP for sample preparation with the exception that sufficient tissue was removed from each fish to allow for five aliquots to be distributed to the participating labs. The tissue was removed from each fish and ground into a well mixed consistent texture; then divided into five equal aliquots, one for each lab. UDOH provided pre-screened mercury free tubes for each aliquot. The unique sample ID numbers were placed on the tubes and they were then put in the freezer. All instruments used to process each fish were then decontaminated in accordance with the sample preparation SOP before processing the next fish. The fish were then wrapped back in their original foil, placed in a zip-lock baggie and returned to the freezer so tissue would be available if the test needed to be repeated. After all fish had been processed, data recorded, and lab sheets filled out, samples were shipped to the individual laboratories on dry ice.

To identify any contamination during handling, storage, and preparation for analysis, quality control checks were used as these samples were being processed. After decontamination of the crucible used to homogenize the samples, de-ionized water was placed in the crucible and mixed with the pestle. These sample blanks were analyzed to ensure no contamination had been carried over from one sample to the next through the homogenization process. All results from blanks were within the acceptable range. A detailed description of this process is included in the DWQ sample preparation SOP.

Analytical Techniques

There are two commonly used techniques for mercury analysis. The first is the manual cold vapor technique (EPA method 245.6). According to the National Environmental Methods Index (NEMI), "A sample is digested in a glass bottle for 2 hours with a persulfate/permanganate solution under heating. After digestion, the mercury in the sample is reduced to its elemental form with stannous chloride. The concentration of mercury in the sample is determined using a cold vapor atomic absorption (CVAA) spectrometer system." This EPA approved method has been used for many years to determine mercury levels in tissue samples. The EPA and USGS laboratories used this method for the study.

The second technique is known as thermal decomposition (EPA method 7473) and utilizes an automatic mercury analyzer. According to an EPA summary of this method, "Controlled heating in an oxygenated decomposition furnace is used to liberate mercury from solid and aqueous samples in the instrument. The sample is dried and then thermally and chemically decomposed within the decomposition furnace. The decomposition products are carried by flowing oxygen to the catalytic section of the furnace. Here oxidation is completed and halogens and nitrogen/sulfur oxides are trapped. The remaining decomposition products are then carried to an amalgamator that selectively traps mercury. After the system is flushed with oxygen to remove any remaining gases or decomposition products, the amalgamator is rapidly heated, releasing mercury vapor. Flowing oxygen carries the mercury vapor through absorbance cells positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance is measured at 253.7 nm as a function of mercury concentration." The

UDOH laboratory used this thermal decomposition method, as did Texas A&M and the Arizona Department of Health Services. EPA used both the cold vapor and thermal decomposition methods.

All participating laboratories followed established QA/QC procedures. Sample blanks were analyzed, as well as spiked samples and duplicates. Standard reference materials with known concentrations of mercury were analyzed to determine percent recovery. All results were within acceptable ranges. Laboratory Standard Operating Procedures (SOP) for each method include specifics on required QA/QC measures. The UDOH Method 7473 SOP is attached as Appendix A.

Data Summary

Results were received from the laboratories by UDWQ and compiled. The following table shows data results measured in ug/g wet weight.

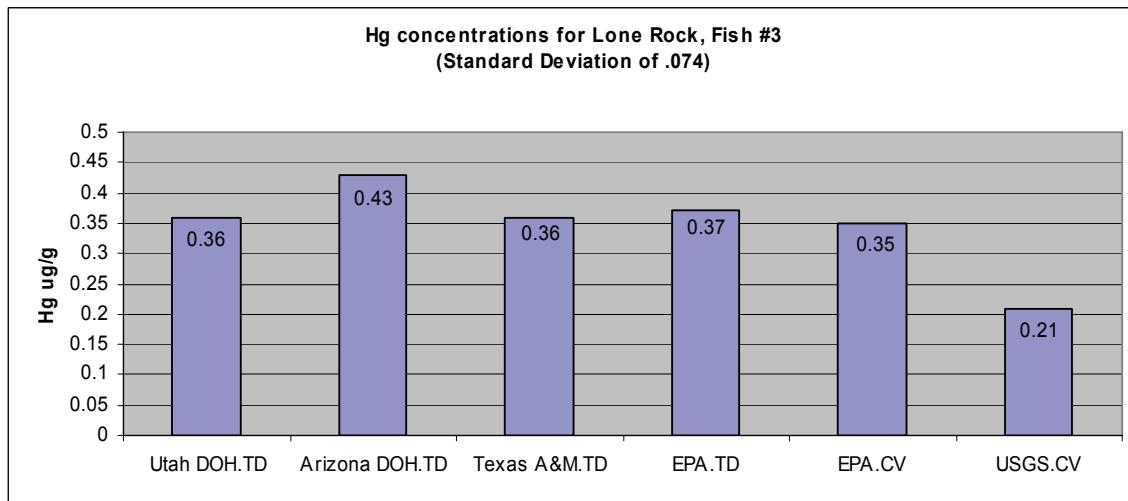
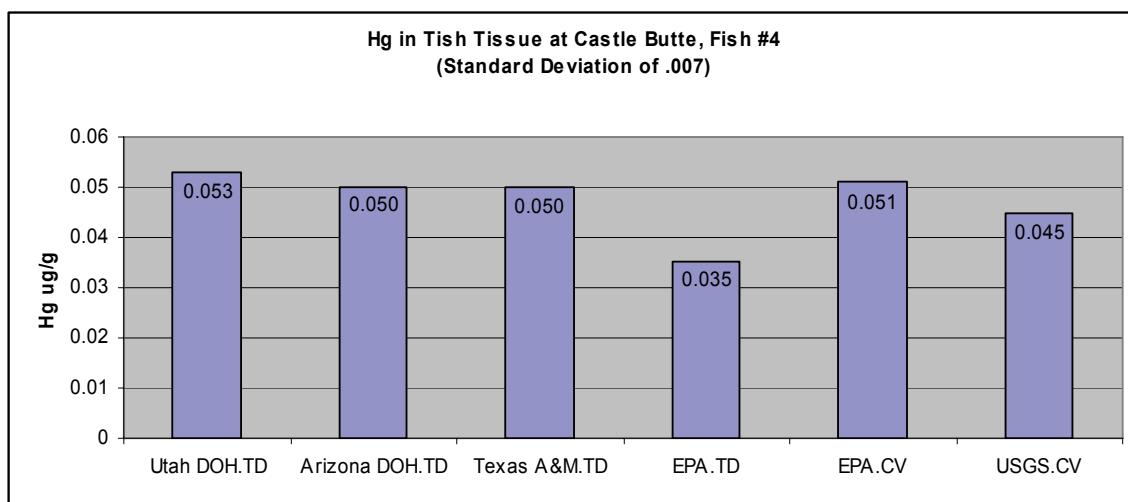
Sample ID	Site Description	Thermal Decomposition				Cold Vapor	
		Utah DOH	Arizona DOH	Texas A&M	EPA	EPA	USGS
5952470STB01	LAKE POWELL - 200 M E OF LONE ROCK	0.21	0.20	0.21	0.22	0.18	0.12
5952470STB02	LAKE POWELL - 200 M E OF LONE ROCK	0.36	0.43	0.36	0.37	0.35	0.21
5952470STB03	LAKE POWELL - 200 M E OF LONE ROCK	0.37	0.31	0.33	0.33	0.31	0.16
5952470STB04	LAKE POWELL - 200 M E OF LONE ROCK	0.18	0.17	0.16	0.17	0.16	0.10
5952470STB05	LAKE POWELL - 200 M E OF LONE ROCK	0.37	0.39	0.34	0.35	0.31	0.20
5952631STB06	LAKE POWELL - SAN JUAN ARM N OF NESKAHI CAN.	0.15	0.15	0.14	0.07	0.15	0.11
5952631STB07	LAKE POWELL - SAN JUAN ARM N OF NESKAHI CAN.	0.20	0.20	0.18	0.19	0.18	0.14
5952631STB08	LAKE POWELL - SAN JUAN ARM N OF NESKAHI CAN.	0.19	0.19	0.20	0.07	0.18	0.13
5952631STB09	LAKE POWELL - SAN JUAN ARM N OF NESKAHI CAN.	0.13	0.12	0.12	0.11	0.12	0.10
5952631STB10	LAKE POWELL - SAN JUAN ARM N OF NESKAHI CAN.	0.19	0.18	0.17	0.13	0.16	0.13
5952748STB01	LAKE POWELL @ RINCON (SOUTHSIDE)	0.09	0.08	0.07	0.08	0.07	0.05
5952748STB02	LAKE POWELL @ RINCON (SOUTHSIDE)	0.07	0.07	0.06	0.07	0.07	0.04
5952748STB03	LAKE POWELL @ RINCON (SOUTHSIDE)	0.11	0.12	0.10	0.11	0.11	0.07
5952748STB04	LAKE POWELL @ RINCON (SOUTHSIDE)	0.10	0.09	0.08	0.08	0.08	0.05
5952748STB05	LAKE POWELL @ RINCON (SOUTHSIDE)	0.08	0.07	0.07	0.07	0.07	0.06
5952913STB06	LAKEPOWELL@GOODHOPEBAY 1/4MIS CASTLE BUTTE	0.10	0.09	0.08	0.07	0.08	0.06
5952913STB07	LAKEPOWELL@GOODHOPEBAY 1/4MIS CASTLE BUTTE	0.11	0.11	0.10	0.08	0.09	0.08
5952913STB08	LAKEPOWELL@GOODHOPEBAY 1/4MIS CASTLE BUTTE	0.07	0.07	0.06	0.05	0.06	0.04
5952913STB09	LAKEPOWELL@GOODHOPEBAY 1/4MIS CASTLE BUTTE	0.05	0.05	0.05	0.04	0.05	0.05
5952913STB10	LAKEPOWELL@GOODHOPEBAY 1/4MIS CASTLE BUTTE	0.12	0.10	0.11	0.10	0.11	0.08

Based on the results reported back to UDWQ it appears that the cold vapor technique generally yields slightly lower values. This is in agreement with Butala and others as referenced. The EPA Region 8 lab utilizes a Nippon mercury analyzer for thermal decomposition analysis. According to Dr. Stephen Butala with UDOH, many

analysts nationwide have noted that the Nippon analyzer may produce lower results than the Milestone instrument, but have also emphasized they have yet to see sufficient studies which support that hypothesis. The USGS noted that their results were obtained under non-optimal conditions. They prefer beginning with more sample material, thus, the lower values observed do not necessarily indicate a problem with their analysis. It should be noted that the amount of tissue provided was problematic for at least two labs and prevented these labs from obtaining optimal results.

Standard deviations between labs are low, showing a great deal of precision between the laboratories. For the thermal decomposition method, standard deviations range from 0 to 0.06 ug/g. For the cold vapor method they ranged from 0.01 to 0.11 ug/g. When considering both methods together, they range from 0.01 to 0.07.

The following charts compare mercury concentrations from both analytical methods for a given site and sample ID. They demonstrate lowest (best case) and highest (worst case) standard deviations observed when considering all values.



Regression analysis indicates high correlation between the labs, with r^2 values ranging from 0.91-0.99. The lowest value of 0.91 is likely driven by outliers resulting from EPA's low values on samples B06 and B08. These results are over a factor of 2 different from the other values. The data set was small so all values were included. In a comparison of the two different methods used by the EPA laboratory, both techniques yielded similar results with $r^2 = 0.88$. This regression line is most likely pulled down by the influence of the two above mentioned low values, but still shows that overall neither method yielded consistently higher or lower results. UDWQ is aware that when using r^2 values, it is generally assumed that one of the variables must be independent. In comparing two laboratories this is not the case, but the analysis is still helpful in looking at the overall correlation.

Average concentrations of mercury found in the fish tissue ranged from 0.05-0.38 ug/g. The EPA criterion set for safe fish consumption is 0.3 mg/kg. Based on this study, three of the twenty fish analyzed were above that criterion. All three were taken from the same location on the lake. A working group of stakeholders from Lake Powell including representatives from the state governments of Arizona and Utah, the Navajo Nation, EPA, USGS and the National Park Service will further analyze all fish tissue data collected for Lake Powell and make recommendations at a later time.

Conclusions

Overall, the UDOH laboratory gave results greater than 90% similar to other laboratories in the region. Most of the differences observed between the labs were most likely inherent in the different techniques used. Based on this study as well as internal QA/QC programs undertaken by the UDOH lab, DWQ concludes that the analytical ability of UDOH is representative when compared with other certified laboratories.

UDWQ will continue mercury monitoring of fish statewide in an attempt to identify elevated levels in fish tissue. Results from Utah's monitoring efforts will be posted on the DWQ web site at (www.waterquality.utah.gov) in order to keep the public well informed on this issue.

Acknowledgments

The Division of Water Quality would like to acknowledge and sincerely thank the cooperating laboratories for their assistance with this project. In particular, the EPA Region 8, USGS Boulder Colorado, and the Arizona Dept. of Health Services laboratories conducted analyses free of charge for UDWQ.

For more information on mercury issues in Utah visit:

<http://www.deq.utah.gov/Issues/Mercury/index.htm>

Reference

Butala, S.J.M., Scanlan, L.P. and Chaudhuri, S,N., "A detailed Study of Thermal Decomposition, Amalgamation/Atomic Absorption Spectrophotometry Methodology for the Quantitative Analysis of Mercury in Fish and Hair"

State of Utah, Dept. of Environmental Quality, Division of Water Quality. Standard Operating Procedure for Collection and Preparation of Fish Tissue Samples for Mercury Analysis.

State of Utah, Department of Health Laboratories. Standard Operating Procedure for Analysis of Mercury In Solids and Solutions by Thermal Decomposition, Amalgamation, And Atomic Absorption Spectrophotometry.